International Journal of Agriculture and Animal Production
ISSN 2799-0907
Vol: 04, No. 01, Dec 2023 - Jan 2024
http://journal.hmjournals.com/index.php/IJAAP
DOI: https://doi.org/10.55529/ijaap.41.24.33

Study of the Release of Agricultural Sulfur and Sulfur Associated with Natural Gas under the Influence of Different Temperatures, Incubation Times and Soil Texture

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Received: 02 August 2023 **Accepted:** 18 October 2023 **Published:** 01 December 2023

***Abstract:** laboratory experiment was carried out to study the effect of temperature (25, 35, and 45 °C) and incubation duration (15, 30, 45, 60, 90, and 120 days) with the addition of two sulfur sources (agricultural sulfur and sulfur associated with natural gas) at a level of 2000 mg S kg^{-1} in dissolved sulfur soil concentration in sandy loam and clay loam soils, with choosing the best temperature to be applied in the kinetic model of sulfur in soil. The temperature and incubation duration results indicated an increase in dissolved sulfur in the agricultural sulfur treatment in both study soils. Also, the 35 °C treatment gave the highest dissolved sulfur compared to the other temperatures, and the incubation period of 120 days recorded the highest amount of dissolved sulfur released. The dual interaction treatment of the sandy loam soil at a temperature of 35 °C and the fertilizer source (agricultural sulfur) gave the largest values of dissolved sulfur in the soil solution, which reached 12.60 mmol S L^{-1}. While clay loam soil at a temperature of 35 °C gave agricultural sulfur the highest values, amounting to 30.68 mmol S L^{-1}.*

***Keywords:** Dissolved Sulfur, Agricultural Sulfur, Associated with Natural Gas, Temperatures, Incubation Periods.*

1. INTRODUCTION

Sulfur is an important element in complete and balanced nutrition for crops and has gained more prominent attention in recent years because it is considered the fourth essential nutrient for plant growth after nitrogen (N), phosphorus (P), and potassium (K). Crops need it in quantities similar to phosphorus and magnesium (Parakhia *et al.*, 2016), as sulfur plays an important role in the vital functions of plants. Its importance is evident through its participation

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in multiple metabolic processes. It is also necessary for the synthesis of amino acids such as cysteine, cystine, and methionine, and it has an important role in the formation of CoASH, vitamins, and the formation of Ferredoxin, which is a powerful reducing agent. It is one of the components of the electronic transport chain for light reactions in the process of photosynthesis, and sulfur is also involved in creating defense mechanisms in plants against pests and diseases and tolerance to drought and pollution with heavy metals (Rossini *et al.*, 2018) and (Narayan *et al.*, 2022) .Sulfur needs to be oxidized to sulfate to be available for plants by various groups of soil microorganisms, most notably genera of Bacteria *Thiobacillus sp.*, and this process is affected by environmental conditions and the physical and chemical properties of the soil, which affect the microorganism groups in it (Degryse *et al*., 2020). The oxidation of sulfur in the soil depends mainly on the chemical composition of the fertilizer, the degree of its decomposition, the time of addition, the abundance of microbial groups, and some physical and chemical soil properties such as soil texture, temperature, soil moisture, content and type of organic matter, and soil pH, which affect the release and release of sulfur in the soil (Kulczycki, 2021 and Zhao *et al*., 2022).
Global sulfur resources were estimated at 25×10^9 tons, of which 4.0% was elemental sulfur, 4.1% in sulfide ores, 83.6% in coal, 3.0% in crude oil, and 5.3% in natural gas (Nehb and Vydra, 2005), and the estimated reserve represents from the sulfur deposits in Iraq are the largest known reserve in the world, ranging between 250-100 million tons of sulfur (Hassan and Zarraq, 2022). Through good management of this element and its use in agricultural techniques, environmental pollution resulting from sulfur emissions associated with extraction operations can be eliminated. oil and gas.

2. MATERIALS AND METHODS

Soil samples were collected randomly and in composite samples at the end of October 2021 from the surface layer, 0-30 cm from two sites with different characteristics in Basra Governorate, the first in the Al-Barjisiyah area (Ts) with coordinates 30°22'02.5"N 47°34'24.2" E and the second in the Medina district (Tc) with coordinates 30°56'39.9"N 47°11'09.5" E. Soil samples were brought to the laboratory, air-dried, then ground and passed through a sieve with a diameter of 4 mm to study some physical properties of the soil according to (Black, 1965) (Table 1) and some chemical properties of the soil according to (Richards, 1954, Jackson, 1958, and Page *et al*., 1982) (Table 2).

Table (1): Some physical properties of the two study soils

Soil symbol	**pH**	**EC**	**Dissolved ions in soil solution**							
			Ca^{+2}	**Mg^{+2}**	**Na^{+}**	**K^{+}**	**SO_4^{-2}**	**Cl^{-}**	**CO_3^{-}**	**HCO_3^{-}**
		dsm^{-1}	**mmol L^{-1}**							
Ts	7.93	2.71	5.62	4.23	4.48	0.59	0.98	18.27	0.00	2.45
Tc	7.79	8.63	8.46	7.79	48.22	3.27	12.42	52.35	0.00	5.19

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Table (2): Some chemical properties of the two study soils

Soil symbol	pH	EC	Dissolved ions in soil solution							
			Ca^{+2}	Mg^{+2}	Na^{+}	K^{+}	SO_4^{-2}	Cl^{-}	CO_3^{-}	HCO_3^{-}
		ds m^{-1}	mmol L^{-1}							
Ts	7.93	2.71	5.62	4.23	4.48	0.59	0.98	18.27	0.00	2.45
Tc	7.79	8.63	8.46	7.79	48.22	3.27	12.42	52.35	0.00	5.19

Soil symbol	CEC	Organic carbon	Organic matter	$CaCO_3$	Ions available in the soil			
					N	P	K	S
	cmol + Kg^{-1}	gm Kg^{-1} soil			mg Kg^{-1} soil			
Ts	7.41	3.54	6.10	169.16	1.12	8.09	39.58	48.85
Tc	23.47	24.71	42.60	445.28	21.62	13.68	197.23	454.58

Agricultural sulfur fertilizer produced by the Mishraq Sulfur General Authority and associated with natural gas produced by R.S.K. Company was used. Some characteristics of the sulfur sources were estimated in the Department of Physics / College of Science / University of Basrah using Field-emission scanning electron microscope (FE-SEM) (High-resolution imaging Technology) type Nova NanoSEM 450 Table (3) and Figure 1 (a and b).

Table (3): Chemical analysis of the two sulfur sources used in the study

sulfur sources	Sulfur	Carbon	Oxygen	Sodium	Silicon	Mercury
	%					
Agricultural sulfur	**98.33**	**1.67**	**-**	**-**	**-**	**-**
Sulfur associated with natural gas	**85.56**	**1.75**	**6.38**	**1.42**	**2.12**	**2.77**

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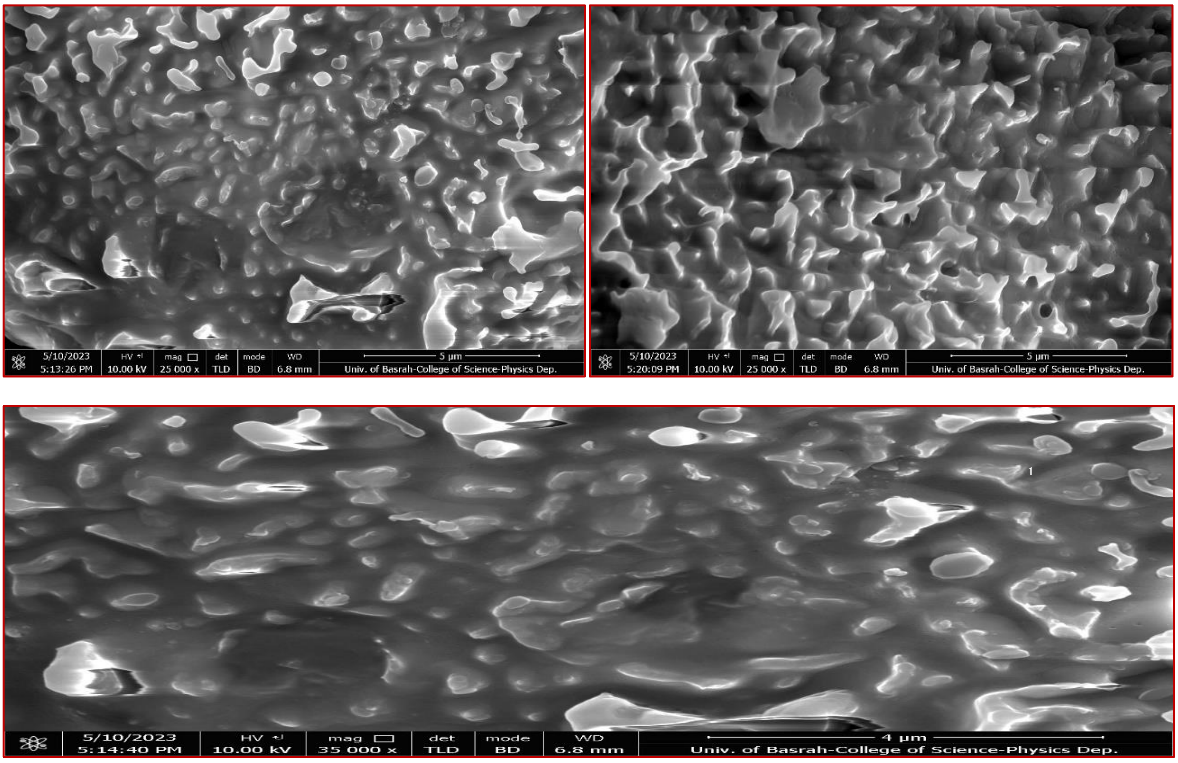

Figure 1 (a): The high-resolution imaging using an FE-SEM scanner for agricultural sulfur

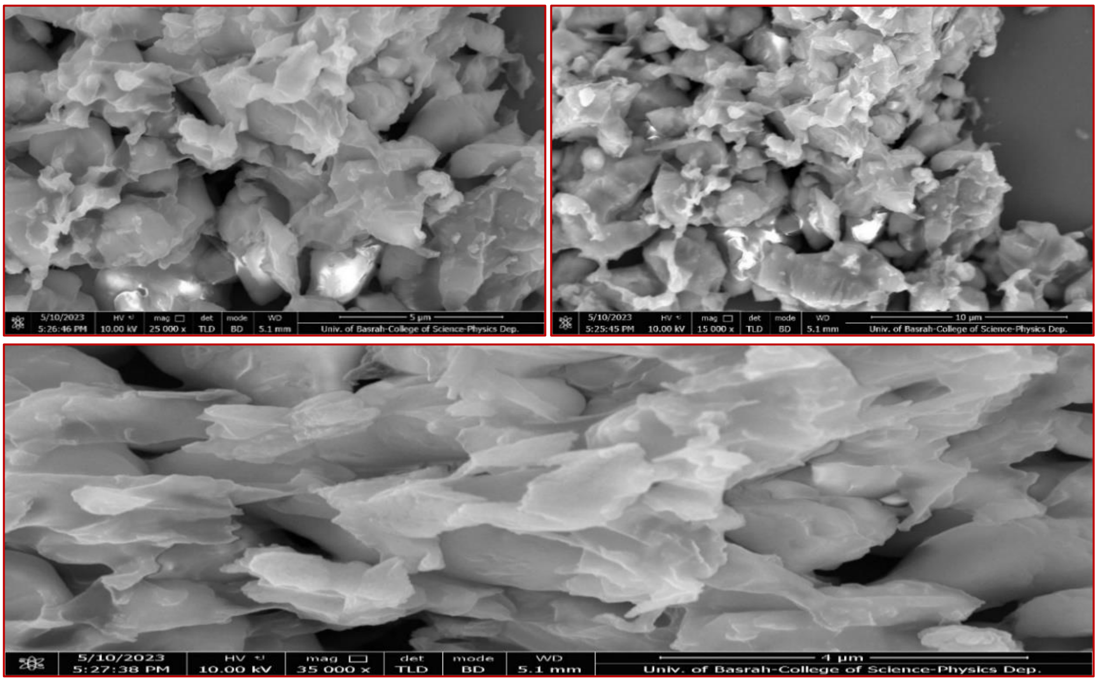

Figure 1 (b): The high-resolution imaging using an FE-SEM scanner for Sulfur associated with natural gas

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The laboratory experiment included studying the effect of two sources of sulfur (agricultural sulfur Sa and sulfur associated with natural gas Sg), soil texture (sandy loam Ts and clay loam Tc), temperature 25, 35 and 45 °C with incubation periods of 15, 30, 45, 60, 90 and 120 days on Concentration of dissolved sulfur in the soil solution by adding a sulfur level of 2000 mg S kg^{-1} soil and irrigating the soil to the field capacity limits throughout the incubation period. After the end of each incubation period, the dissolved sulfur in the soil was estimated to choose the temperature that best describes the release of sulfur.
The experiments were conducted with three replicates as a factorial experiment and in a completely randomized design (CRD) using analysis of variance through the statistical program SPSS V.23. The averages of the coefficients were compared using the least significant difference (RLSD) at the probability level of 0.05.

3. RESULTS AND DISCUSSION

The results showed the effect of the sulfur source on the dissolved sulfur in the soil solution under the two soils of the study (Figure 2). Agricultural sulfur was significantly superior ($P > 0.05$) compared to the sulfur associated with the gas in both soils of the study. The percentage of superiority was close in both soils, around 7%, and this is due to the effect of the general characteristics of the sulfur source, such as variation in the sizes of sulfur particles and their surface area exposed to the activity of sulfur-oxidizing organisms (Table 3) and Figure 1 (a and b), this is consistent with the findings of Degryse *et al.* (2016a) that the process of sulfur oxidation depends on the shape and size Sulfur particles added to the soil.

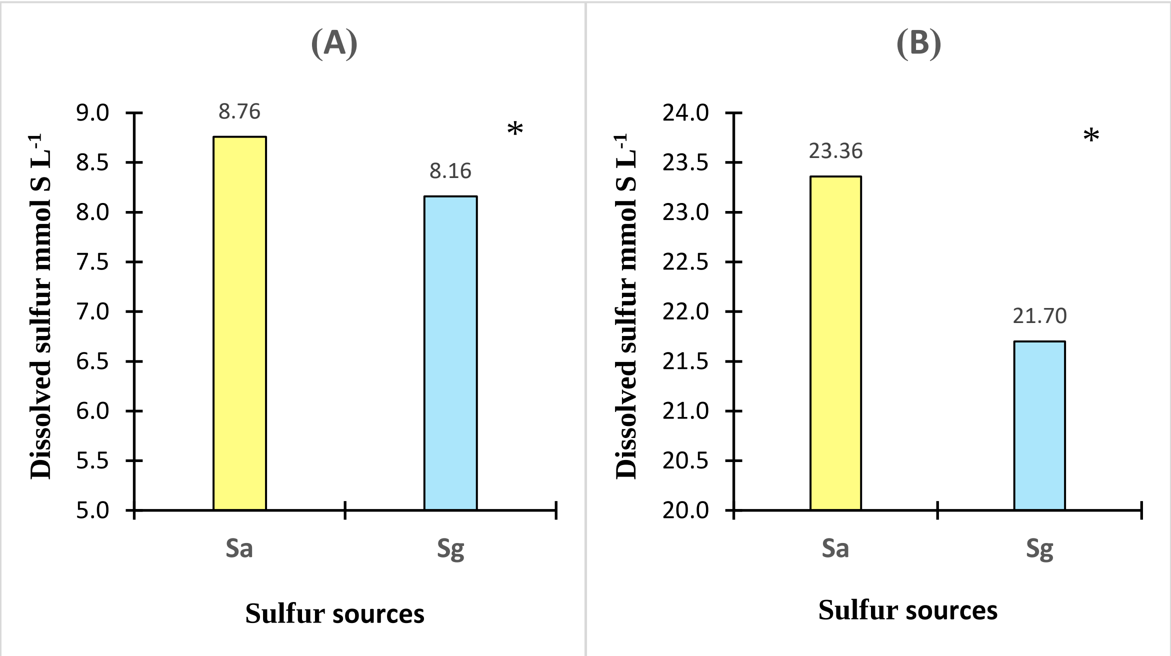

Figure (2): The effect of the sulfur source on the rate of dissolved sulfur in the soil: A) Sandy loam and B) Clay loam

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Figure (3) shows the difference in the effect of temperature on the rate of dissolved sulfur in the two study soils. The concentration of dissolved sulfur increased significantly at a temperature of 35 °C compared to a temperature of 25 °C, reaching 23.36 and 22.63 mmol S L^{-1} in the clay loam soil and 9.14 and 8.47 mmol S L^{-1}, respectively, in the soil. sandy loam sand, we find that the sulfur concentration subsequently decreased to 21.62 and 7.78 mmol S L^{-1} at a temperature of 45 °C for both soils, respectively. This is because the sulfur oxidation process is mainly a biological process that depends on the activity of sulfur-oxidizing microorganisms. These microorganisms have an optimum temperature at which they can operate with maximum effectiveness. Therefore, we find that the temperature of 35 °C represents the appropriate temperature for the activity of these microorganisms, and it is behind the increase in oxidation at this temperature (Zhi-Hui *et al*., 2010 and Kumar *et al*., 2020) .

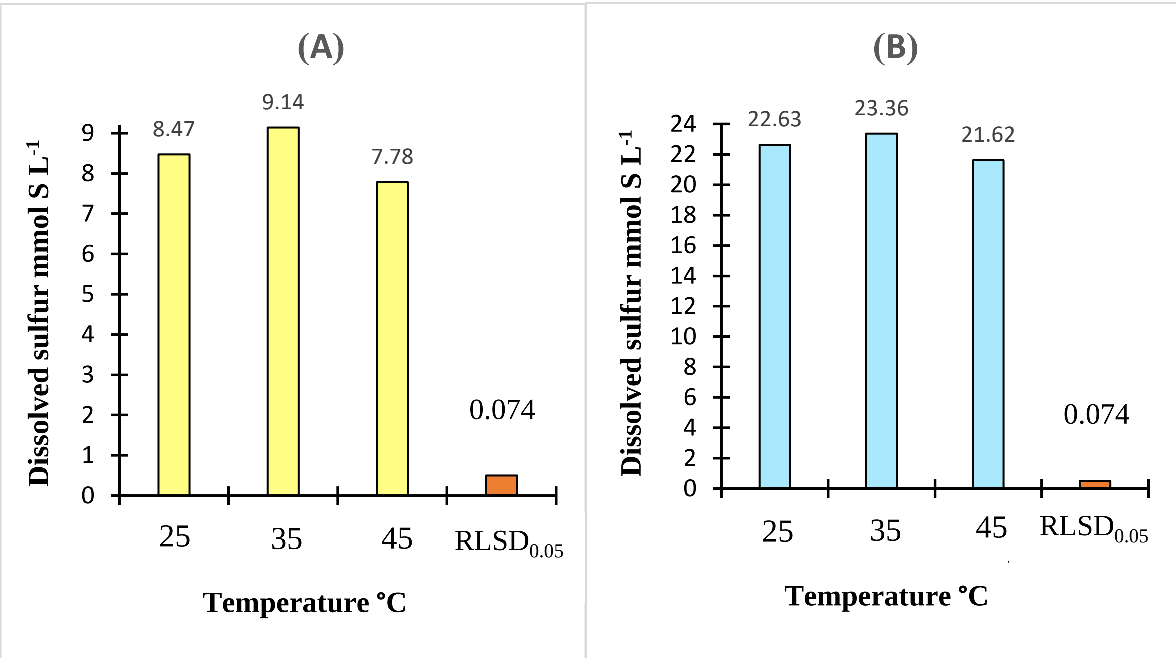

Figure (3): The effect of temperature on the rate of dissolved sulfur in the soil: A) Sandy loam B) Clay loam

Figure 4 shows that there is a significant increase in the concentration of sulfur in both soil textures with time, as the dissolved amount of sulfur increased by 162.87% and 88.62% for the sandy loam and clay loam soils, respectively, after 60 days of incubation period compared to the 15-day incubation period, then the percentage of increase decreased. After 90-120 days of incubation, compared to a period of 60 days, especially in sandy loam soil. The reason for the increase in sulfur concentration over time is the availability of a sufficient amount of organic matter on which microorganisms work, thus an increase in the activity and work of organisms in oxidation and the availability of sufficient time for that. The reason for the decrease in the increase the expulsion after that may be due to a decrease in the activity of sulfur-oxidizing microorganisms due to the continuous consumption of organic matter in the soil and increased competition among them (Antonius *et al*., 2019).

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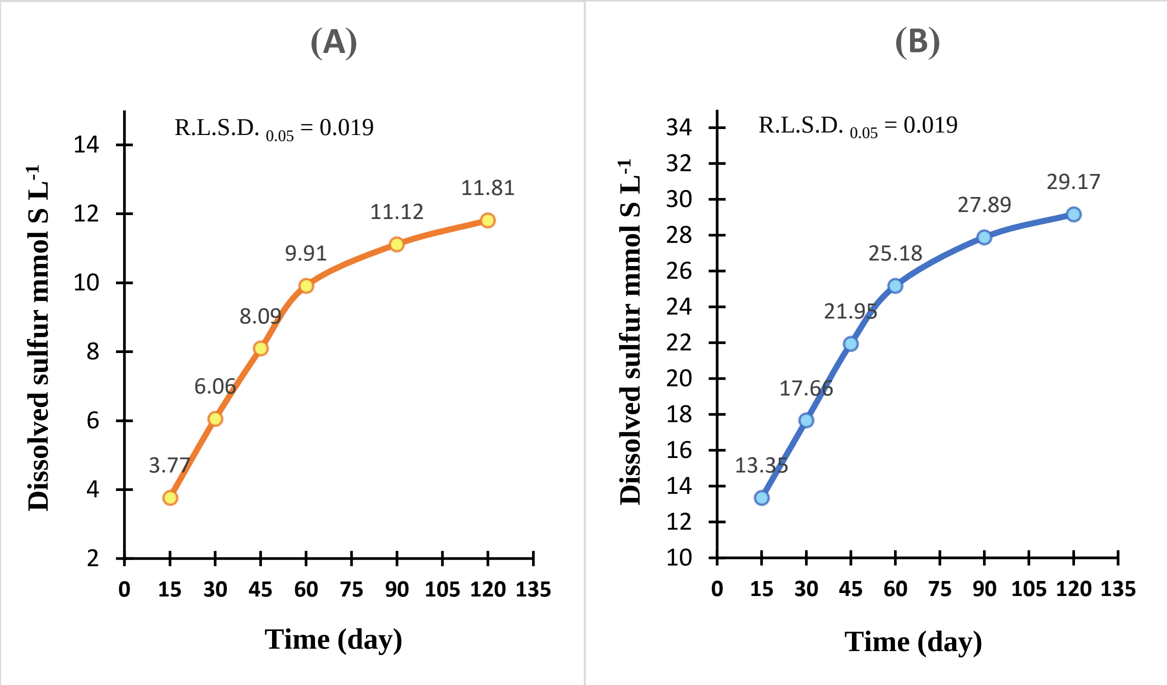

Figure (4): The effect of incubation duration on the rate of concentration of dissolved sulfur in the soil A) Sandy loam B) Clay loam

Figure 5 indicates that there are statistical differences ($P > 0.05$) for the binary interaction between the sulfur source and the temperature for both soil textures in the average concentration of dissolved sulfur, as the Sa treatment at a temperature of 35 °C recorded the highest values, reaching 9.48 and 24.09 mmol S L^{-1} for the two soil textures. The sandy loam and clay loam soils were compared to the rest of the treatments, while the Sg treatment at the same temperature recorded 8.79 and 22.62 mmol S L^{-1}, respectively. The reason may be due to the availability of a suitable biological environment to increase sulfur oxidation due to the good properties of agricultural sulfur compared to the sulfur associated with the gas natural. Table (3) and Figure 1 (a and b) and the optimum temperature for the activity of sulfur-oxidizing microorganisms (Montjabi *et al*., 2019).

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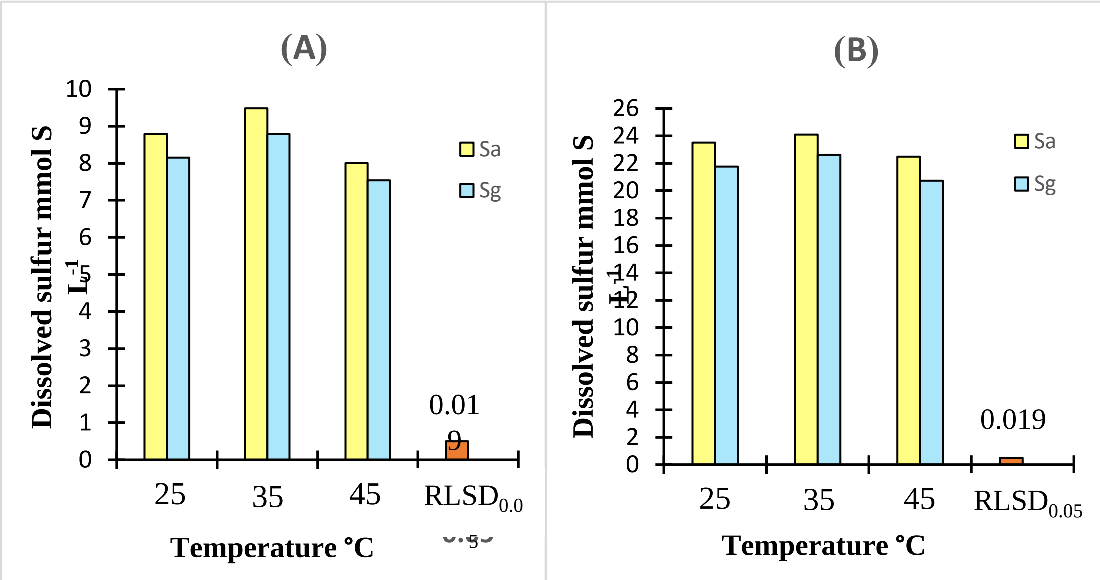

Figure (5): The effect of the binary interaction between the sulfur source and temperature on the rate of dissolved sulfur in the soil A) sandy loam B) clay loam

The results of the binary interaction of the sulfur source and incubation duration showed that there was a significant increase in the concentration of dissolved sulfur with increasing incubation duration for both fertilizer sources and soils (Figure 6). Agricultural sulfur (Sa) was superior in dissolved quantity to the sulfur associated with the gas at all incubation durations. The percentage increase is 3.44% and 8.47% for sandy loam and clay loam soils, respectively, after an incubation period of 120 days between the two fertilizer sources.

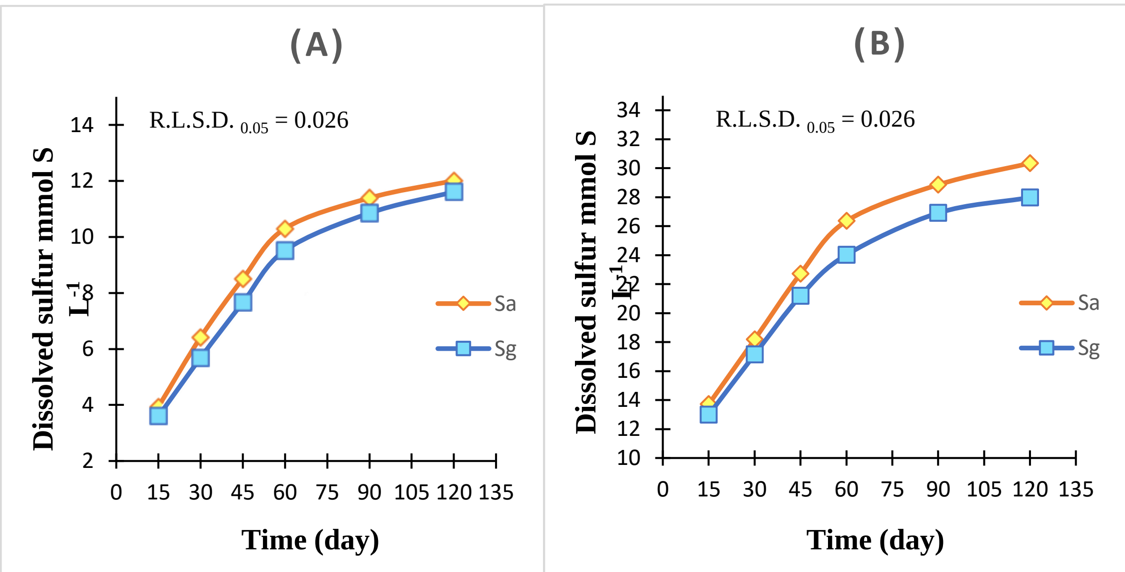

Figure (6): The effect of the binary interaction between the source of sulfur and the duration of incubation on the rate of dissolved sulfur in the soil A) Sandy loam B) Clay loam

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Figure 7 shows a case of binary interaction of temperature and incubation duration in the dissolved amount of sulfur. The concentration of dissolved sulfur increased with increasing incubation duration in both soils, with statistical differences at the level of 0.05, and the concentrations of dissolved sulfur reached 12.40, 11.90, and 11.12 mmol S L^{-1} in the soil. Sandy loam and 30.23, 29.32, and 27.94 mmol S L^{-1} in clay loam soil after 120 days of incubation at temperatures of 25, 35, and 45 °C, respectively. There is also a variation in the effect of temperature on dissolved sulfur, as the temperatures took the following sequence in increasing the release of sulfur and thus increasing its solubility in the solution: 35 > 25 > 45 °C. This leads to a cumulative increase in the oxidized amount of sulfur fertilizer with increasing time, as well as the optimum temperature of the activity of sulfur-oxidizing organisms (Solberg *et al*., 2005) and thus its reflection on the sulfur dissolved in the soil solution.

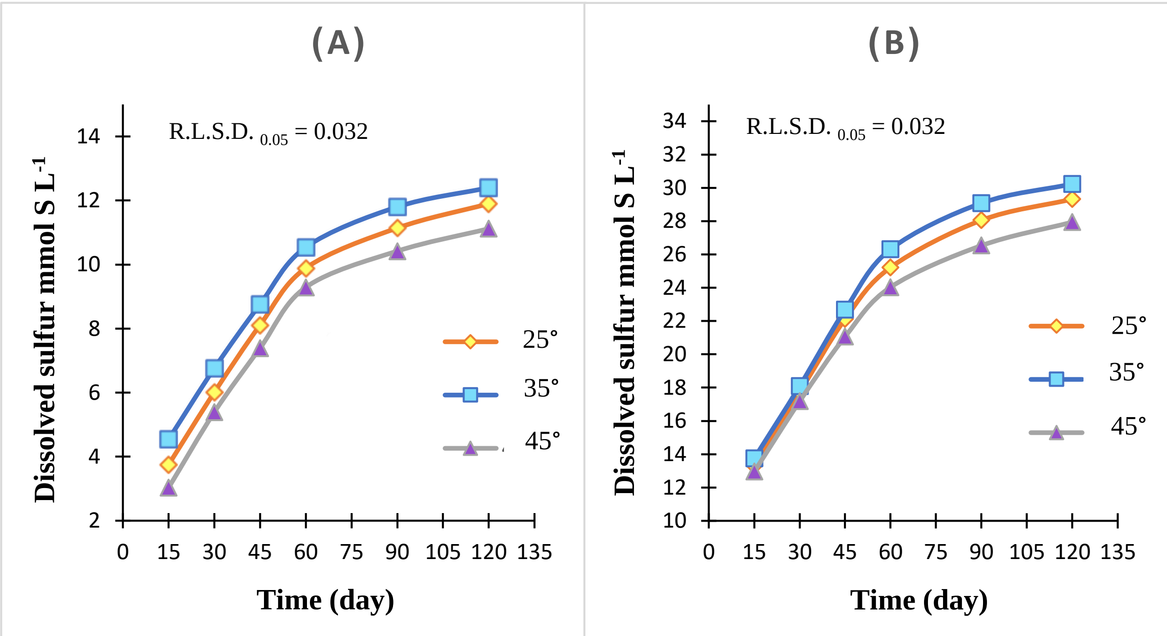

Figure (7): The effect of the binary interaction between temperature and incubation duration on the rate of dissolved sulfur in the soil: A) Sandy loam B) Clay loam

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